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Polyphosphazenes are among the most versatile of all polymers. This is a consequence of the unique properties of the phosphorus-nitrogen backbone and the ease with which a wide range of different side groups can be introduced mainly by macromolecular substitution, but also by the polymerization of different "monomers". This field has reached a stage where the fundamental chemistry now allows the design and synthesis of a broad range of new materials that are valuable for properties such as elasticity, high refractive index, liquid crystallinity, ferroelectric-, NLO-, and photochromic attributes, and for uses as solid ionic conductors, biomedical microencapsulation polymers, and materials with controlled surface properties.

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MACROMOLECULAR AND MATERIALS DESIGN USING POLYPHOSPHAZENES

by

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Prepared for Publication in ACS Symposium Series

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MACROMOLECULAR AND MATERIALS DESIGN USING POLYPHOSPHAZENES

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Polyphosphazenes are among the most versatile of all polymers. This is a consequence of the unique properties of the phosphorus-nitrogen backbone and the ease with which a wide range of different side groups can be introduced mainly by macromolecular substitution, but also by the polymerization of different "monomers". This field has reached a stage where the fundamental chemistry now allows the design and synthesis of a broad range of new materials that are valuable for properties such as elasticity, high refractive index, liquid crystallinity, ferroelectric-, NLO-, and photochromic attributes, and for uses as solid ionic conductors, biomedical microencapsulation polymers, and materials with controlled surface properties.

Inorganic-Organic Polymers as Components of New Materials

Materials science covers a very broad range of substances within the four main classical categories of ceramics, metals, semiconductors/electro-optical solids, and petrochemical polymers. Most of the examples in the first three categories are inorganic in composition, while the last is mainly organic. All four have advantages and disadvanges. For example, the totally inorganic materials are heavy, often britttle, and difficult to fabricate. On the other hand, conventional polymers are tough and easy to fabricate but are unstable at elevated temperatures and lack many of the interesting electrical and optical properties of the inorganic materials.

The main concept behind the current interest in inorganic or inorganic-organic polymers is that they may provide a means for the preparation of new materials that combine the advantages and minimize the disadvantages of the classical materials. Thus, the long term interest lies in the design and synthesis of new polymers that have combinations of properties such as ease of fabrication coupled with ceramic-like thermal stability, toughness combined with electrical conductivity, elasticity plus biological compatibility, etc.

It is also believed that the incorporation of inorganic elements into macromolecules will generate property combinations that will be tunable over a wide range by alterations in the types of inorganic elements present and by changing the ways in which the inorganic components are incorporated into the structure. In order to be able to realize this potential it is necessary to understand the structural features of polymers that are responsible for their special properties and the properties to be expected from the presence of certain inorganic elements. The following paragraphs provide a summary of these factors.
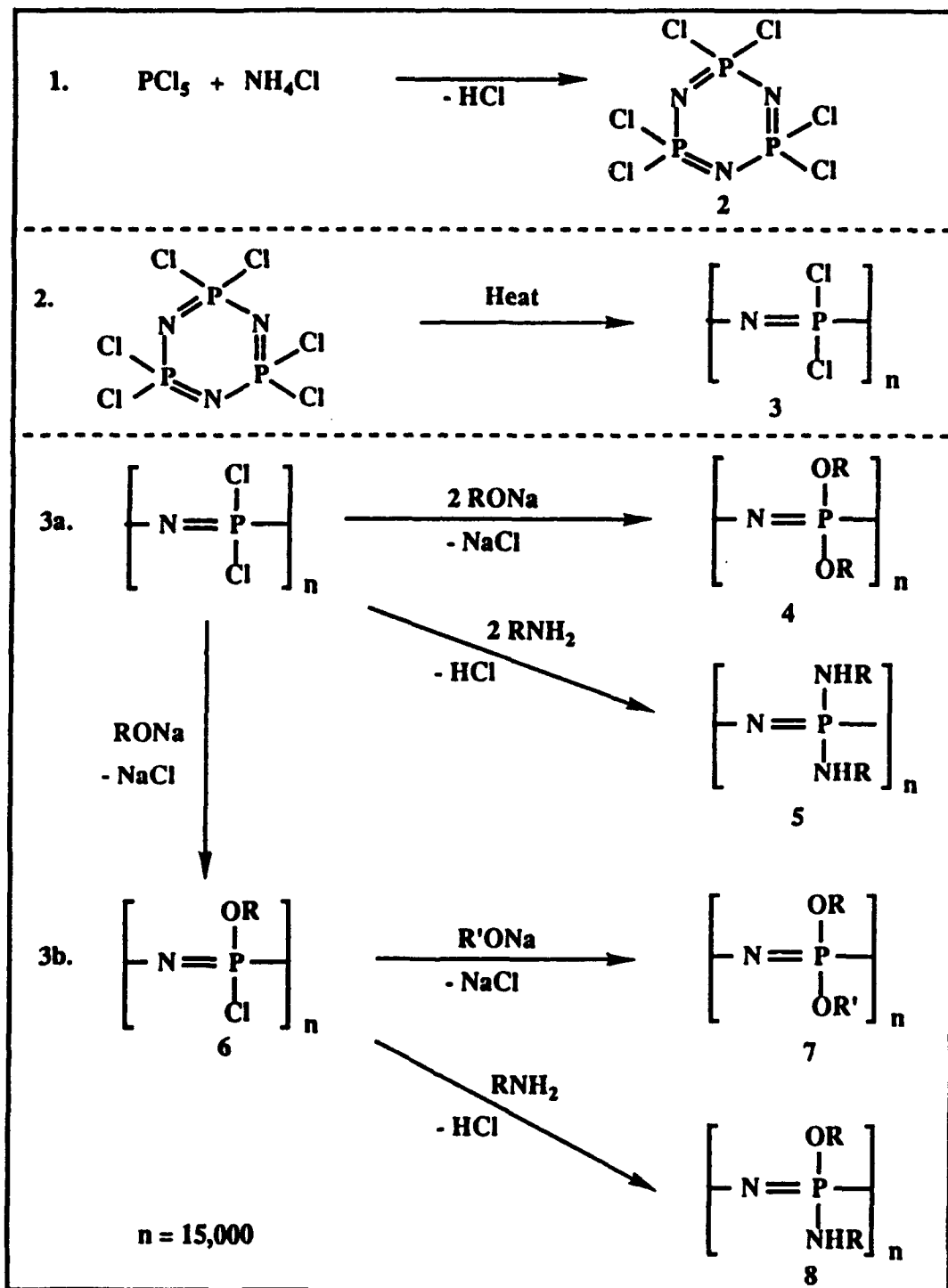
Types of Macromolecular Structure.

Polymers can be found that are linear, macrocyclic, lightly branched, dendritic, lightly crosslinked, heavily crosslinked, ladder-like, or sheet-like in structure, and each geometry gives rise to a different set of properties. Furthermore, the properties are also influenced by the degree of polymerization of the molecules. Species that contain only a few monomer units (say 10 to 100 repeating units) lack the entanglement capabilities of higher polymers and therefore lack strength, toughness, and ease of fabrication. Such species are of only limited usefulness as materials, although they may serve as precursors to ceramics. Genuine polymeric properties become apparent only when 1000 or more repeating units are present

Perhaps the next most important determinant of properties is the degree to which the system is crosslinked. Uncrosslinked polymers are usually soluble in some solvent, although the existence of crystalline domains (brought about by molecular symmetry and efficient interchain packing) may make the process of dissolving difficult. Nevertheless, the existence of an average of only 1.5 crosslinks per chain is sufficient to totally prevent the separation of the polymer molecules in a liquid medium. The polymer may swell in a suitable liquid, but it will not dissolve. Increases in the number of crosslinks per chain will progressively reduce the degree of swelling, until eventually the system will be an unswellable, three-dimensionally crosslinked ceramic. Light crosslinking may favor elasticity by preventing individual chains fron sliding past each other when the bulk material is stretched. Heavy crosslinking not only confers resistance to solvents, but also provides rigidity and strength.

Macromolecular geometry, degree of crosslinking, and repeating unit symmetry affect other properties too. An important characteristic of any polymeric material is the way in which the physical properties change with temperature. An amorphous polymer will be a glass at temperatures below its glass transition temperature (Tg), but a rubbery material above that temperature, changing to a semi-fluid gum at still higher temperatures. The glass transition temperature is a measure of two factors - the ease of torsional flexibility of both the backbone and the side groups, and the degree of "free volume" generated by the shape of the side groups. Backbone segments that contain bonds with low barriers to torsion will often yield low Tg values. For example, some of the lowest Tg values known (-100°C to -130°C) are associated with polymers that possess silicon-oxygen or phosphorus-nitrogen backbone bonds, because these bonds have very low barriers to torsion. Thus, the incorporation of inorganic elements into the backbone structure provides opportunities to control the Tg over a very wide temperature range, and in turn to control whether the polymeric material will be an elastomer, a glass, or a gum throughout a particular temperature range.

Efficient chain packing, and the resultant presence of microcrystallites, will cause the elastomeric phase to be replaced by a so-called thermoplastic phase which is flexible, but has dimensional integrity under moderate stress. This phase gives way to a liquid or gum-like phase at temperatures above the melting point of the crystallites. The presence or absence of crystallinty depends on the shape and size of the side groups, on the regularity of their disposition along the chain, and on the absence of extensive chain branching or crosslinking. Side groups that can form ordered structures in the liquid-like phase may give rise to liquid crystallinity.
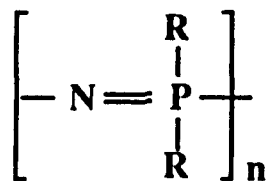
Scheme I

1. $PCl_5 + NH_4Cl \xrightarrow{- HCl}$ **2**

2. **2** $\xrightarrow{\text{Heat}}$ $\left[-N=P\begin{smallmatrix} Cl \\ | \\ Cl \end{smallmatrix} \right]_n$ **3**

3a. $\left[-N=P\begin{smallmatrix} Cl \\ | \\ Cl \end{smallmatrix} \right]_n$ $\xrightarrow[- NaCl]{\text{2 RONa}}$ $\left[-N=P\begin{smallmatrix} OR \\ | \\ OR \end{smallmatrix} \right]_n$ **4**

$\xrightarrow[- HCl]{\text{2 RNH}_2}$ $\left[-N=P\begin{smallmatrix} NHR \\ | \\ NHR \end{smallmatrix} \right]_n$ **5**

$\xrightarrow[- NaCl]{\text{RONa}}$

3b. $\left[-N=P\begin{smallmatrix} OR \\ | \\ Cl \end{smallmatrix} \right]_n$ **6** $\xrightarrow[- NaCl]{\text{R'ONa}}$ $\left[-N=P\begin{smallmatrix} OR \\ | \\ OR' \end{smallmatrix} \right]_n$ **7**

$\xrightarrow[- HCl]{\text{RNH}_2}$ $\left[-N=P\begin{smallmatrix} OR \\ | \\ NHR \end{smallmatrix} \right]_n$ **8**

n = 15,000

The presence of inorganic elements in the main chain and in the side group structure can affect the properties through all of these influences and can impart other characteristics as well. For example, properties such as flame retardance, electrical conductivity, biological compatibility, resistance to high energy radiation, or the appearance of ferroelectric behavior, may all be generated by the incorporation of inorganic elements.

The largest class of inorganic-organic polymers is found in the polyphosphazenes (1). At least 300 diferent polyphosphazenes are known at the present time. Thus, this system is an excellent example of the structural diversity and range of properties that can be generated by the incorporation of elements other than carbon into a polymer backbone.

$$\left[-N = \underset{\underset{R}{|}}{\overset{\overset{R}{|}}{P}} - \right]_n$$
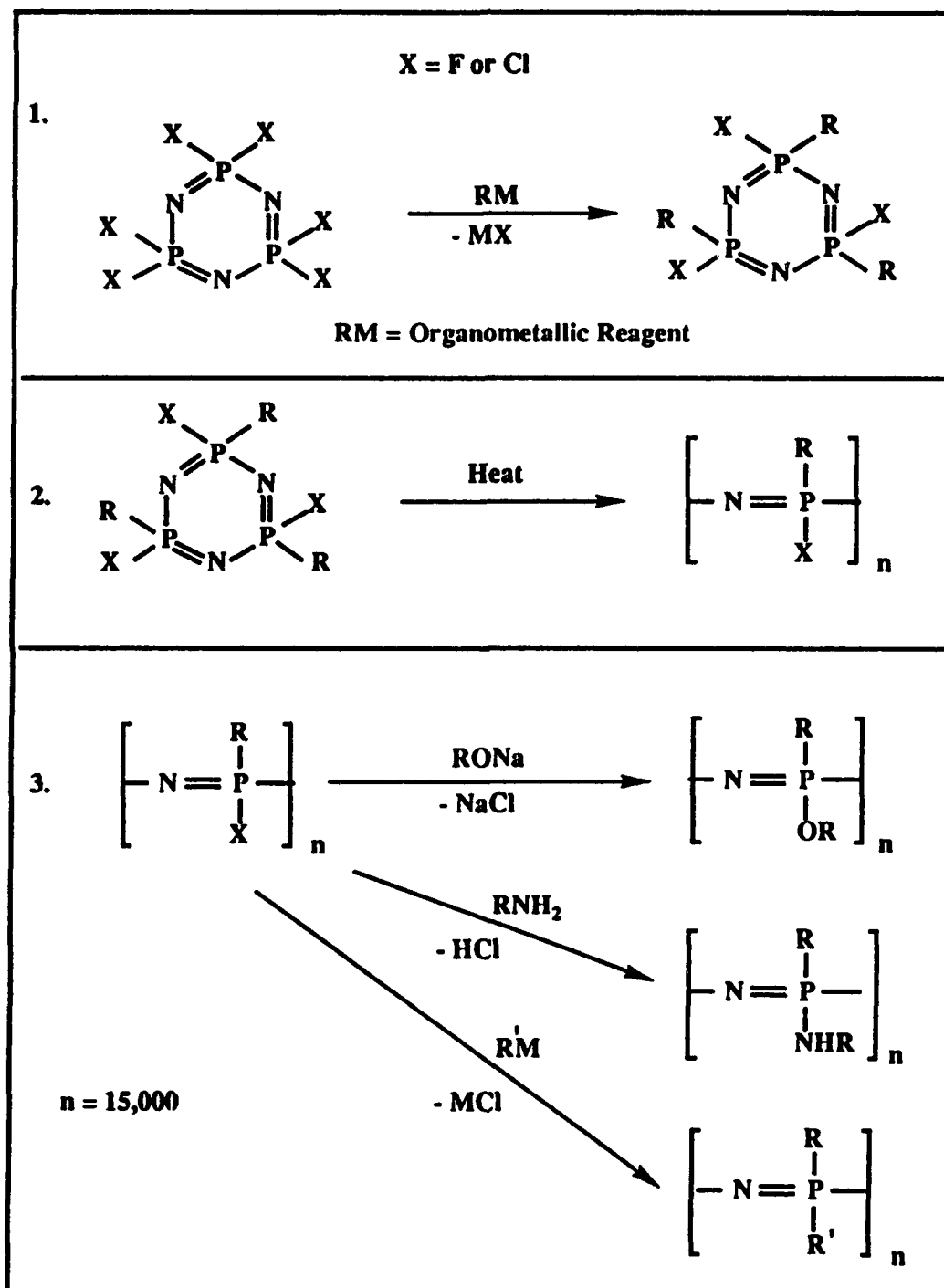
1

Introduction to Polyphosphazenes

The most widely used synthesis route to stable poly(organophosphazenes), first developed in our program, is illustrated in Scheme I (1-4). The ring-opening polymerization of hexachlorocyclotriphosphazene (2) [or its fluoro-analogue $(NPF_2)_3$)] leads to the formation of a high molecular weight poly(di-halogenophosphazene) such as 3. This polymerization takes place in the molten trimer or in solution. Solution state polymerizations are facilitated by the use of Lewis acid initiators (5, 6).

Polymer 3 is a reactive macromolecular intermediate for a wide range of halogen replacement reactions (Scheme I) (4, 7, 8). Many of these reactions are S_N2-type substitutions, although a few have S_N1 character. Replacement of the halogen atoms in 3 by most organic or organometallic side groups yields hydrolytically-stable derivative polymers. These reactions have led to the synthesis and study of a broad range of stable polyphosphazenes, the properties of which are frequently improvements over those of widely used totally-organic macromolecules (4).

Further structural diversity can be accomplished by the simultaneous or sequential replacement of the halogen atoms in $(NPCl_2)_n$ or $(NPF_2)_n$ (see structures 6-8) by two or more different nucleophiles or by chemical reactions carried out on the organic, inorganic, or organometallic side groups without involvement of the polymer skeleton. Moreover, alkyl, aryl-, or organometallic side groups can be linked to the phosphorus atoms at the level of the cyclic trimeric "monomer". Subsequent ring-opening polymerization then provides a pathway to even more polymer structures, as shown in Scheme II.

Scheme II

X = F or Cl

1.

$$X_2P(=N)N = P X_2 \xrightarrow[\text{- MX}]{\text{RM}} \text{(ring with X, R substituents)}$$

RM = Organometallic Reagent

2.

$$\text{(ring)} \xrightarrow{\text{Heat}} \left[-N = \underset{\underset{X}{|}}{\overset{\overset{R}{|}}{P}} - \right]_n$$

3.

$$\left[-N = \underset{\underset{X}{|}}{\overset{\overset{R}{|}}{P}} - \right]_n \xrightarrow[\text{- NaCl}]{\text{RONa}} \left[-N = \underset{\underset{OR}{|}}{\overset{\overset{R}{|}}{P}} - \right]_n$$

$$\xrightarrow[\text{- HCl}]{\text{RNH}_2} \left[-N = \underset{\underset{NHR}{|}}{\overset{\overset{R}{|}}{P}} - \right]_n$$

$$\xrightarrow[\text{- MCl}]{\text{R'M}} \left[-N = \underset{\underset{R'}{|}}{\overset{\overset{R}{|}}{P}} - \right]_n$$

n = 15,000

A further variant of this preparative protocol involves the synthesis of polymers that contain phosphorus, nitrogen, and a third element in the main chain. For example, we have recently prepared the first poly(carbophosphazenes) and poly(thiophosphazenes) via the chemistry shown in Schemes III and IV (9, 10). Manners has reported the synthesis of poly(thionylphosphazenes) using the same approach (11).

Alternative methods of polyphosphazene synthesis also exist (12-15) and several of these approaches are discussed elsewhere in this volume. Finally, chemistry conducted at the surface of polyphosphazenes allows the tailoring of those surfaces to achieve the development of specific chemical, physical, or biological characteristics (16-20).

Inherent in all this work is the idea that these processes allow a rational control to be exercised over macromolecular and materials structure. This has led to the development of a wide range of structure-property relationships that form the basis for producing useful new materials. The following examples illustrate these principles.

Control of the Glass Transition Temperature (Tg) Through Skeletal and Side Group Changes

The polyphosphazene skeleton is one of the most flexible chains yet studied in polymer chemistry. T_g values as low as -105°C have been measured, and this is an indication of a very low barrier to torsion of the backbone bonds. This property is attributed to the absence of side groups on every other skeletal atom, to the wide P-N-P bond angle (which minimizes intramolecular interactions), and to the participation of phosphorus 3d orbitals in the d_π -p_π unsaturation of the skeleton. However, the introduction of carbon atoms into the skeleton raises the Tg by roughly 20°C when the same side groups are present, and this probably reflects the higher barrier to torsion of C=N compared to P=N double bonds (9).

Superimposed on the low Tg properties of the backbone is the influence of the side groups. Small or flexible side groups such as -F, -Cl, -OCH$_3$, -OC$_2$H$_5$, -OC$_3$H$_7$, -OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$, -OCH$_2$CF$_3$, etc. impose little or no additional barrier to torsion of the backbone, and the Tg's remain in the -100°C to -60°C region. However, phenoxy groups raise the Tg to -8°C, p-phenylphenoxy- to +93°C, and phenylamino to +91°C. Thus, steric bulk or the capacity for hydrogen bonding brings about a sharp rise in the Tg. The use of different side groups allows the Tg to be tuned over a 200°C temperature range, and this is a powerful design feature.

High Refractive Index, Liquid Crystalline, Ferroelectric, NLO, and Photochromic Side Groups.

Chart I illustrates five polyphosphazenes in which different side groups generate various optical or electro-optical properties.

First, the refractive index of a polyphosphazene can be altered by the introduction of side groups that contain different numbers of electrons. High numbers

Scheme III

POLY(CARBOPHOSPHAZENE) SYNTHESIS

Scheme IV

POLY(THIOPHOSPHAZENE) SYNTHESIS
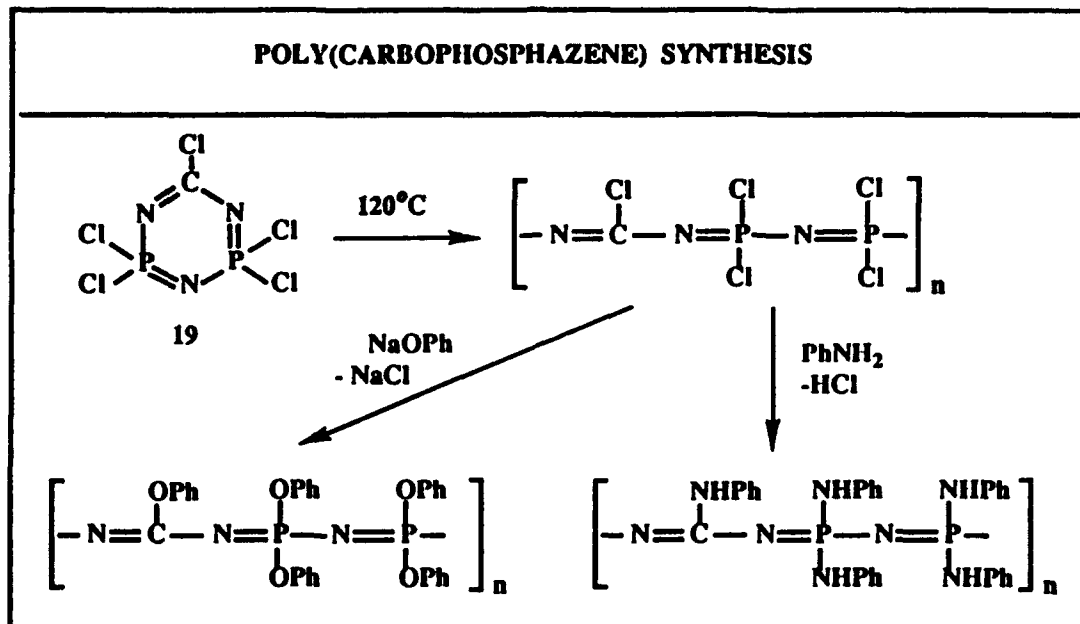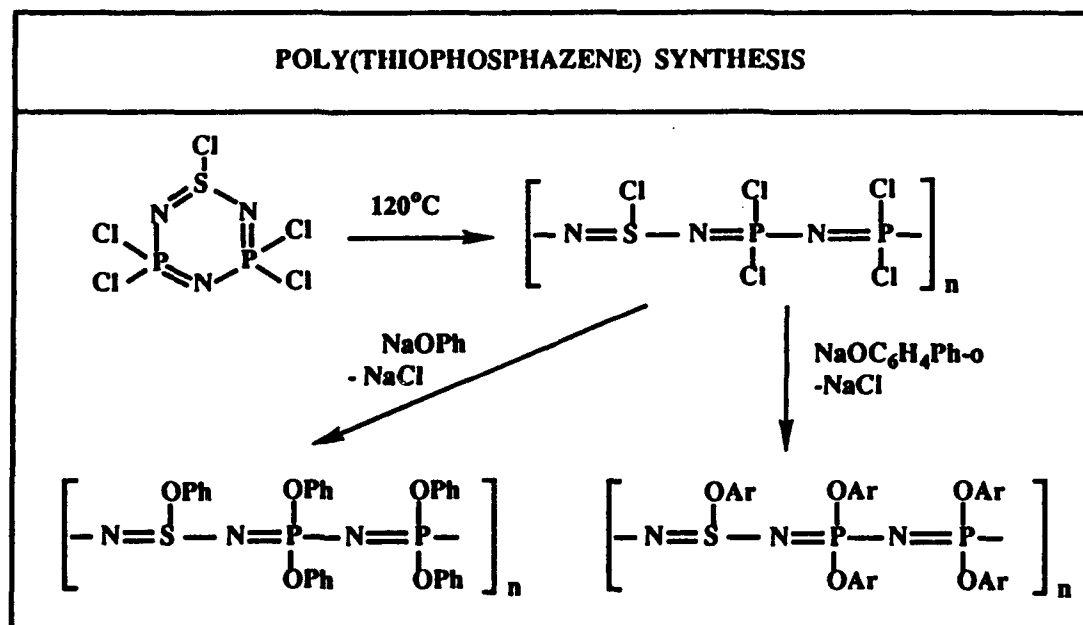
of electrons per side unit yield higher refractive indices. Hence, aromatic or polyaromatic side groups give some of the highest values. Polymer 9 has a refractive index of 1.686 (21) which can be compared, for example, to the value of 1.591 for polystyrene.

Second, the presence of rigid, mesogenic side groups, which can form ordered arrays above the crystallite melting temperature, can give rise to liquid crystallinity (22-28). Structure 10 represents a class of polymers that have this property.

Ferroelectric behavior has been detected for polymer 11, as a consequence of the "chiral smectic-C" structure of the liquid crystalline phase (29). Polymer 12 is a second order nonlinear optical material, the polarizable side groups, in which can be poled in a 10-20 kV electric field to generate χ^2 values in the region on 34-45 picometers per volt (30, 31). Finally, species 13 is a photochromic polymer, which undergoes a spiropyran-merocyanine transformation when exposed to ultraviolet light (32).

Side Groups for Different Crosslinking Processes

The development of reactions for the crosslinking of polyphosphazenes is an important aspect of the materials science of this field. Crosslinking processes play a role in processes as diverse as elastomer formation, stabilization of NLO properties, photolithography, and the formation of hydrogels and organogels. Crosslinking processes fall into two categories--chemically-induced processes, and those brought about by radiation.
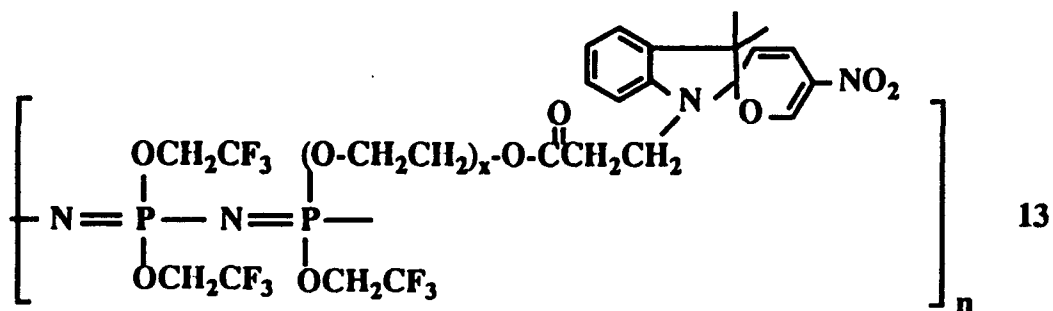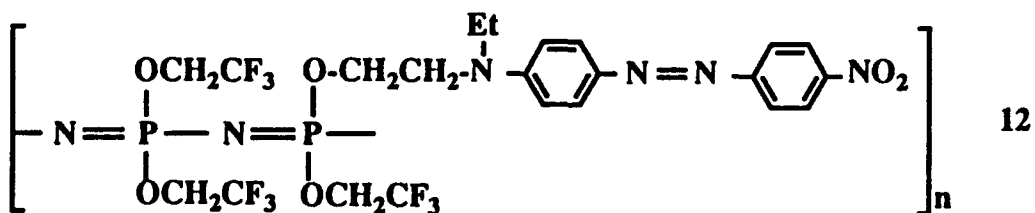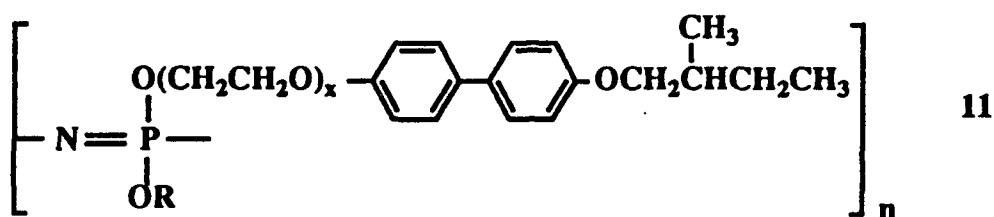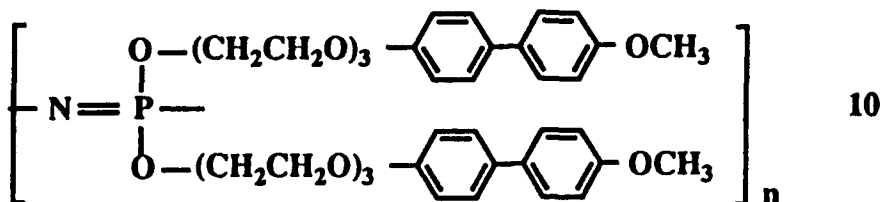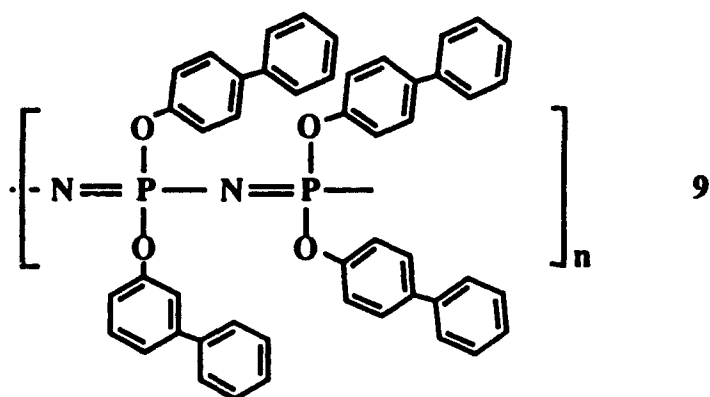
Commercial alkoxy- or aryloxy-phosphazene elastomers contain pendent allyl groups for free radical crosslinking in the final stages of fabrication (33). Methathetical side groups exchange reactions have also been used for crosslinking (34). Chemical crosslinking also plays a critical part in the conversion of several polyphosphazenes to ceramic-type materials. Unless crosslinking takes place at an early stage in the ceramicization process, the individual polymer molecules may depolymerize and the fragments volatilize before a useful material can be formed (Scheme IV).

For example, the n-propylaminophosphazene polymer shown in Scheme V undergoes thermal side group condensation and crosslinking between 250°C and 1000°C to yield phosphorus nitride and graphite (35, 36). The borazine-bearing polyphosphazene depicted in Scheme VI reacts in a similar fashion (37). Amino groups on borazine rings and others linked to the polymer backbone facilitate the crosslinking reactions that are required to prevent depolymerization and fragmentation at elevated temperatures. The initial pyrolysis leads to the formation of phosphorus-nitrogen-boron matrices, and above 1000°C to boron nitride.
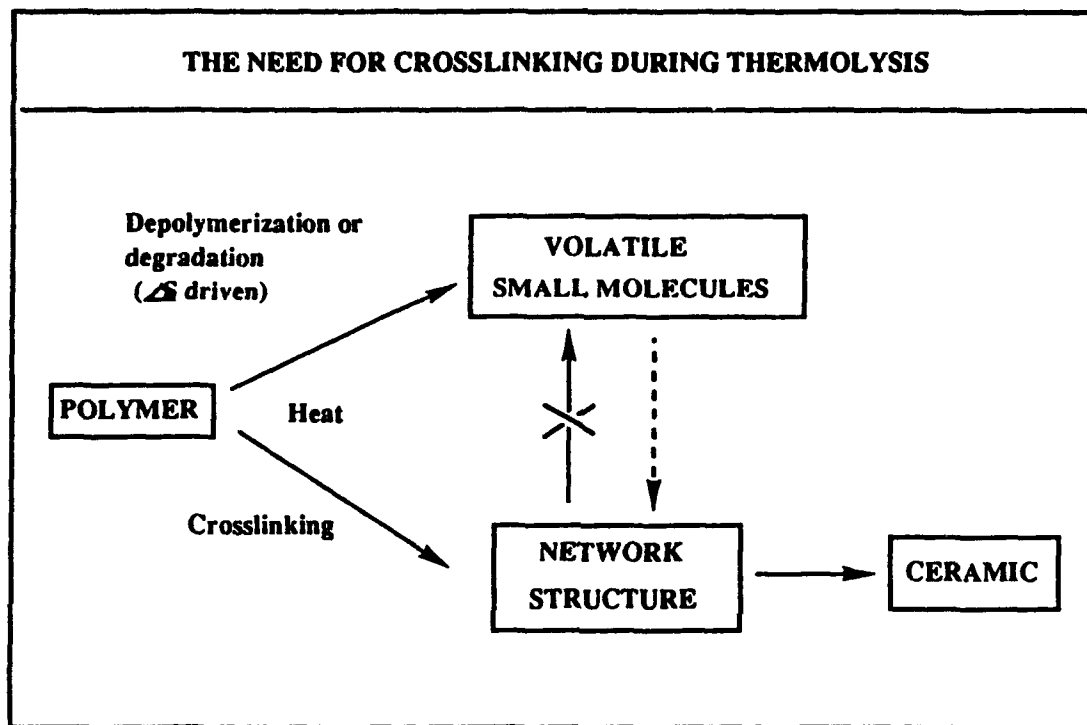
Photo-crosslinking through organic side groups is an important process in polyphosphazene chemistry, especially because the backbone is insensitive to a wide spectrum of high energy radiation. Thus side group crosslinking can be effected without significant backbone cleavage.

Ultraviolet-induced crosslinking has been demonstrated for polyphosphazenes with -OCH2CH2OCH2CH2OCH3 side groups (with and without photosensitizers) (38)

Chart 1

9

$$N=P \text{ — } N=P$$

with substituents O—(biphenyl), O—(biphenyl), O—(phenyl-phenyl) ...

9

$$\left[\begin{array}{c} N=P \\ \end{array} \right]_n$$

O—(CH₂CH₂O)₃—(biphenyl)—OCH₃
O—(CH₂CH₂O)₃—(biphenyl)—OCH₃

10

O(CH₂CH₂O)ₓ—(biphenyl)—OCH₂CHCH₂CH₃
                                              |
                                             CH₃
OR

11

OCH₂CF₃   O-CH₂CH₂-N—(phenyl)—N=N—(phenyl)—NO₂
                              |
                              Et
OCH₂CF₃   OCH₂CF₃

12

OCH₂CF₃   (O-CH₂CH₂)ₓ-O-CCH₂CH₂ ...NO₂
                              ‖
                              O
OCH₂CF₃   OCH₂CF₃

13

Scheme IV

THE NEED FOR CROSSLINKING DURING THERMOLYSIS

Depolymerization or degradation (ΔS driven)

POLYMER

Heat

Crosslinking

VOLATILE SMALL MOLECULES

NETWORK STRUCTURE

CERAMIC

Scheme V

$$\left[-N = \overset{\overset{\displaystyle NHPr}{|}}{\underset{\underset{\displaystyle NHPr}{|}}{P}} - \right]_n \qquad n = 15{,}000$$

- NHPr$_2$ 250-800°C   - NH$_2$Pr

N$_2$

$$\left[-N = \overset{\overset{\displaystyle NHPr}{|}}{\underset{\underset{\displaystyle |}{|}}{P}} - \right]_n$$

NH

$$\left[-N = \overset{\overset{\displaystyle |}{|}}{\underset{\underset{\displaystyle NHPr}{|}}{P}} - \right]_n$$

$$\left[-N = \overset{\overset{\displaystyle NHPr}{|}}{\underset{\underset{\displaystyle NPr}{|}}{P}} - \right]_n$$

$$\left[-N = \overset{\overset{\displaystyle |}{|}}{\underset{\underset{\displaystyle NHPr}{|}}{P}} - \right]_n$$

800-1000°C

Graphite

+

P$_3$N$_5$

Also vapor deposition phosphorus nitrides

Scheme VI

$n = 15,000$

Me_2NH

NH_3

$1000°C$

$(BN)_n$
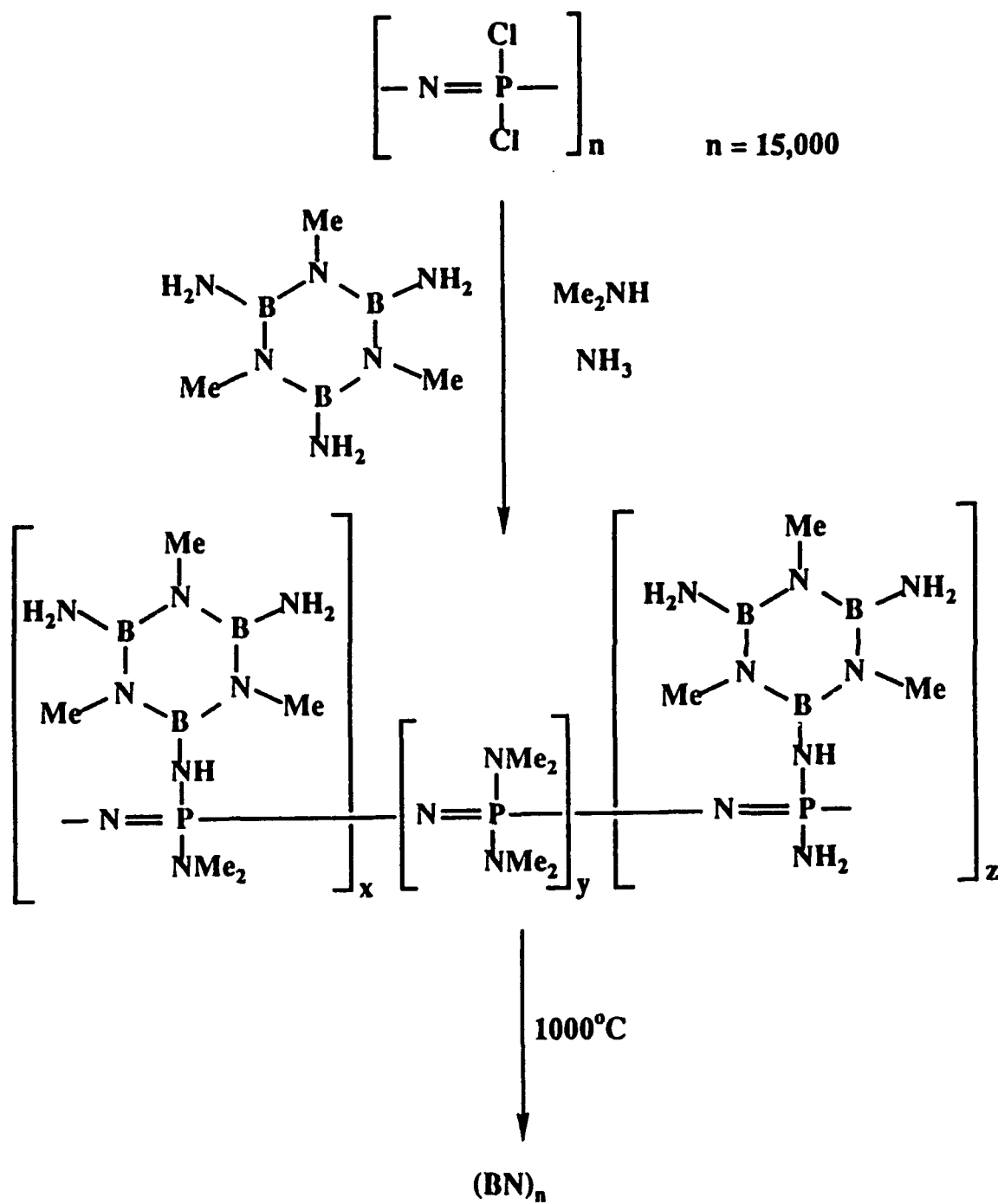
and for the 2+2 cycloadditions of cinnamate and chalcone side groups (*39*). The UV-induced crosslinking of MEEP (14) is important both for the formation of hydrogels and for the dimensional stabilization of solid electrolytes (see later). Cinnamate and chalcone-based crosslinking reactions were developed for the stabilization of NLO activity, but are also potentially useful in photolithography.

Electron beam lithography is possible with allyl-containing arylaminophosphazene polymers (*40*). Work in the group of V. T. Stannett has demonstrated that these species have an e-beam sensitivity and sufficiently high Tg's that they are appropriate for microlithography.

Gamma rays are particularly effective for crosslinking alkyl ether phosphazene polymers such as $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ or $[NP(NHCH_3)_2]_n$ (Scheme VII) (*41-44*).

The pattern is emerging that almost any polyphosphazene with a high loading of aliphatic C-H bonds in the side group system can be crosslinked by exposure to gamma-rays. This is a clean procedure that generates no impurities as side products and allows the degree of crosslinking to be controlled within fine limits by the radiation dose. Perhaps the most effective use of this technique so far is in the crosslinking of MEEP, to be discussed in the following section.
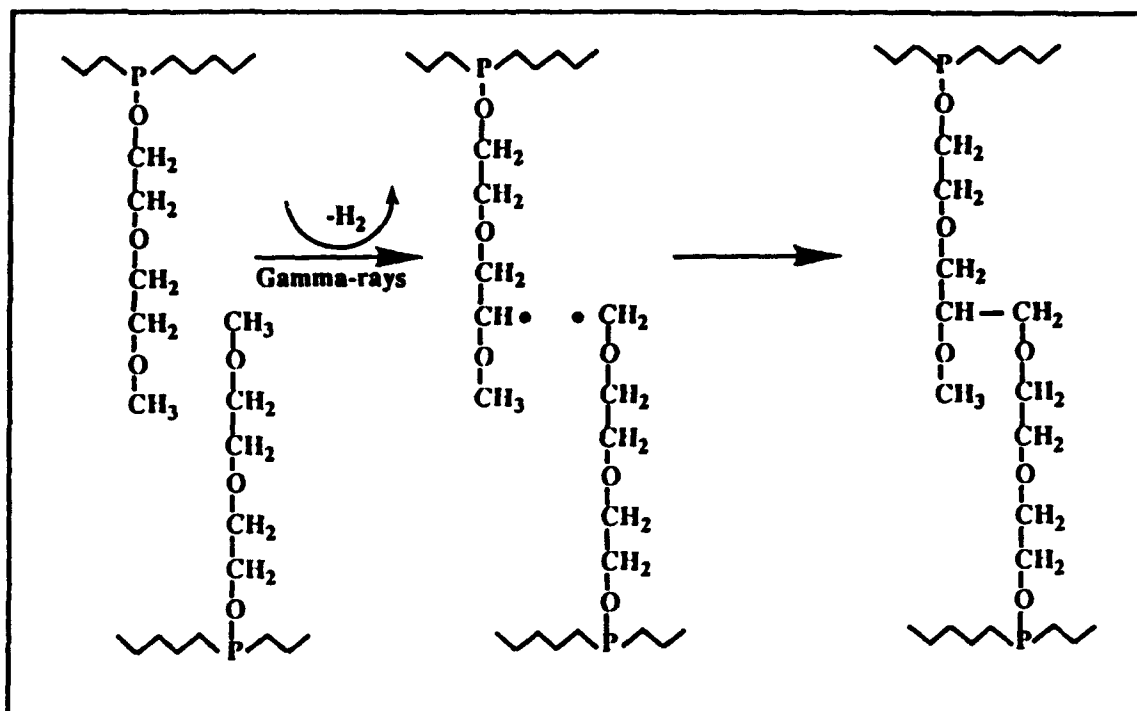
Solid Polymeric Electrolytes Based on Crosslinked MEEP-Type Materials

(a) General Features. The design and development of MEEP (14) as a solid polymeric electrolyte was initiated in 1983-84 through a collaborative program between our research group at The Pennsylvania State University and that of D. F. Shriver at Northwestern University (*45-49*). The possible use of this polymer in lightweight, rechargeable lithium batteries was a driving force for that work.
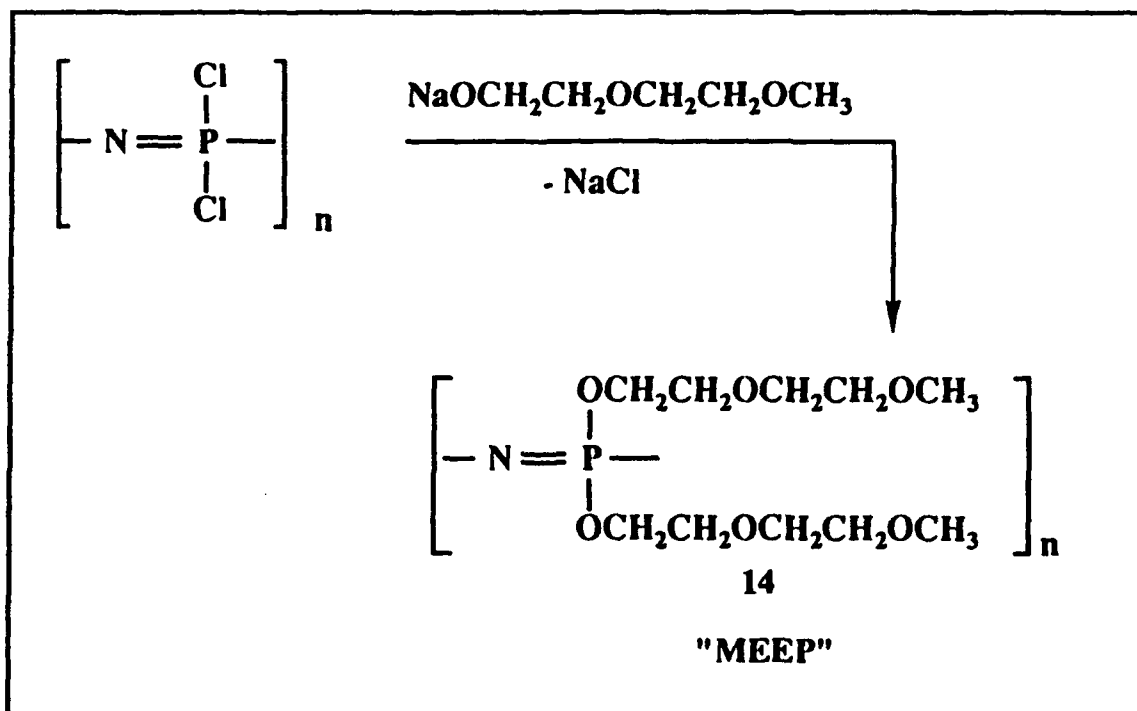
MEEP is synthesized by the process shown in Scheme VIII (*50*), in which poly(dichlorophosphazene) (3), is allowed to undergo chlorine replacement reactions in the presence of the sodium salt of methoxyethoxyethanol in a solvent such as tetrahydrofuran. MEEP is an excellent solid solvent for salts such as lithium triflate. Salts dissolved in this polymer undergo ion-pair separation as a result of coordination of the Li^+ cations by the oxygen atoms of the alkyl ether side groups. In this system the ions can migrate through moving polymer molecules under the pressure of an electric current. Use of this electrolyte in rechargeable lithium batteries is expected to provide an improvement in robustness, safety, and ease of fabrication compared to liquid electrolytes or polymers dissolved in liquid electrolyte systems.

It became clear at an early stage that MEEP has marked advantages as a solid electrolyte matrix over the classical standard in this field, which is poly(ethylene oxide). MEEP has a very low glass transition temperature of -84°C (the temperature below which molecular motion becomes restricted), it is non-crystalline, and has six oxygen atoms per repeat unit for coordination to cations in a way that facilitates ion-pair separation. By contrast, poly(ethylene oxide) contains crystalline domains that impede ion migration, so that electrolytic cells based on this polymer must be heated to 80-100°C before practical conductivities can be obtained. At room temperature, the

Scheme VII

$-H_2$, Gamma-rays

Scheme VIII

$NaOCH_2CH_2OCH_2CH_2OCH_3$

$- NaCl$

$$\left[-N=\overset{\displaystyle OCH_2CH_2OCH_2CH_2OCH_3}{\underset{\displaystyle OCH_2CH_2OCH_2CH_2OCH_3}{P}}- \right]_n$$

14

"MEEP"

conductivity of MEEP-based electrolytes is 2-3 orders of magnitude higher than comparable systems based on poly(ethylene oxide). This difference can be partly overcome by the use of random copolymers of ethylene oxide and propylene oxide, but such copolymers still contain fewer oxygen solvation sites per repeat unit than does MEEP.

The original studies of MEEP-based electrolytes revealed one problem - that the polymer molecules were so flexible that the bulk polymer had a tendency to undergo viscous flow under pressure, thus being prone to slow extrusion from electrolytic cells.

The work described here was designed to overcome this problem by development of methods to crosslink the polymer chains while, at the same ti. avoiding contamination by conductive impurities and maintaining the relatively hi$_b$ room temperature conductivity of MEEP/lithium triflate electrolytes. Crosslinking *after* the formation of the MEEP/lithium triflate films was considered to be an essential prerequisite to allow the fabrication of the electrolyte in the form of large surface area batteries or in intricately shaped devices.

(b) Gamma-Ray Crosslinking. A series of studies carried out in my group by Kwon, Gebura, Riding, Fitzpatrick, and Bennett *(41-44, 51)*. revealed that MEEP is sensitive to crosslinking when exposed to gamma rays. This behavior is a consequence of the high loading of aliphatic carbon-hydrogen bonds (22 per repeating unit), which are especially prone to radiation-induced homolytic cleavage, and this provides a mechanism for intermolecular carbon-carbon bond formation (Scheme VIII). An advantage of this technique is that the degree of crosslinking can be finely controlled by the radiation dose, and no impurities are introduced into the material.

Gamma-radiation crosslinked MEEP swells in water to form hydrogels *(41, 52)*. In the water-free state the polymer does not undergo viscous flow. Conduction experiments carried out by Bennett, Dembek, Allcock, Heyen, and Shriver *(51)* on gamma-ray crosslinked MEEP/lithium triflate films indicated little if any diminution in conductivity following the introduction of an average of one crosslink per 100 repeating units (20 Megarads). Thus, the local segmental motion of the polymer is maintained under these conditions, and the ability of the system to facilitate ion migration is retained.

However, ^{60}Co gamma-ray crosslinking requires the use of specialized facilities, and this constitutes a possible impediment to expanded research on and development of this system.

(c) Ultraviolet Crosslinking Most totally organic polymers are affected detrimentally by exposure to ultraviolet light. Both main chain cleavage and side group free radical reactions are common, and these often lead to a deterioration in materials properties. However, the phosphazene backbone in MEEP is relatively stable to high energy radiation and it resists free radical cleavage processes.

The exposure of films of MEEP to 2200 - 4000 Å ultraviolet radiation results in crosslinking *(38)*. The reaction takes place readily in the presence of photosensitizers such as benzophenone, but also occurs in the absence of added photosensitizers.

Crosslinking can be monitored by changes in the ^1H and ^{13}C NMR spectra and by the degree to which the polymer imbibes solvents without dissolving.

The ultraviolet crosslinking method is inexpensive (compared to gamma-ray irradiation) and yields a dimensionally stable electrolyte uncontaminated with conductive chemical residues. The characteristics are particularly useful in the design and development of rechargeable energy storage devices, several of which have been assembled and tested in our program.

Hydrogels Formed from MEEP

Water-soluble synthetic polymers are quite rare. But they are extremely important in general technology and in biomedicine. One of their most significant properties is their use as precursors to hydrogels. A hydrogel is a water-soluble polymer that, when crosslinked, will imbibe water to a limit defined by the average number of crosslinks per chain. Hydrogels may be 90 or 95% water and are useful as biomedical soft tissue prostheses, soft contact lenses or intraocular lenses, membranes, and as platforms for the immobilization of biologically-active species.

MEEP forms excellent hydrogels when crosslinked by either gamma-ray or UV-irradiation techniques. One application--the immobilization of the enzyme urease--will be described here (53). Solutions of MEEP and urease in water were fabricated into films by water evaporation . These were crosslinked by gamma rays and the system allowed to absorb water to form a hydrogel (see Figure 1). The enzyme molecules could not be extracted from the hydrogels by water, confirming that each enzyme molecule was physically trapped within the polymer matrix and surrounded by water molecules. Exposure of the gels to aqueous solutions of urea indicated that the trapped enzymes retained their ability to convert urea to ammonia. This is a prototype system for the preparation of a wide variety of enzyme "reactors."

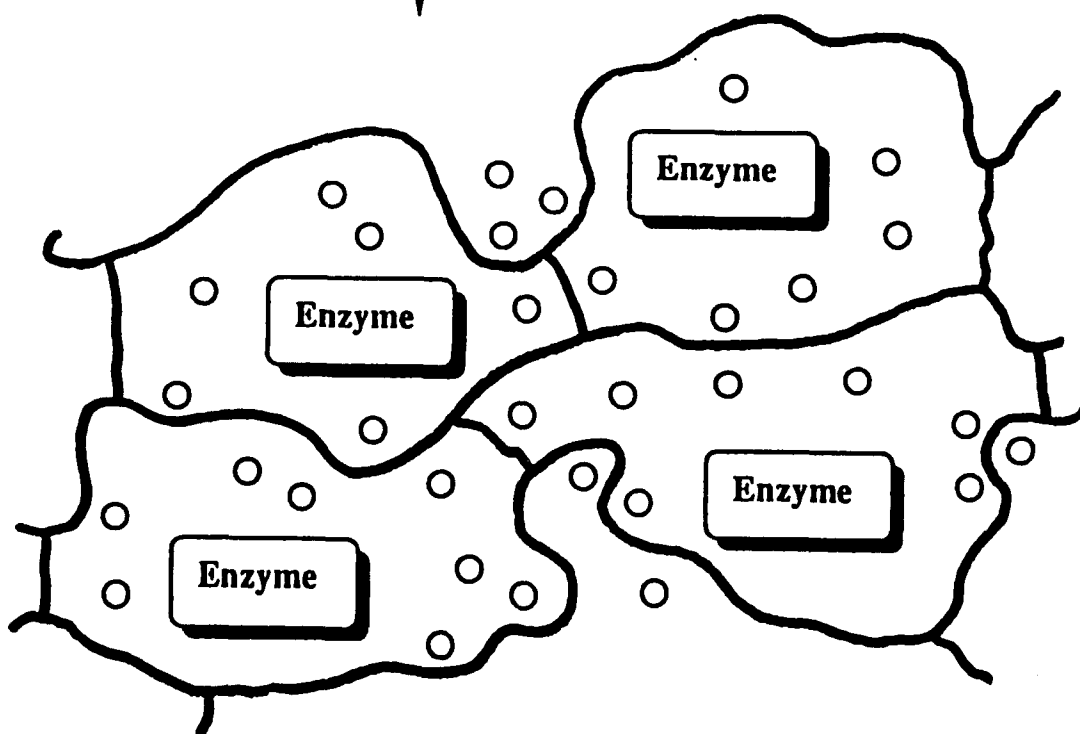## A Polyphosphazene Polyelectrolyte for Biomedical Microencapsulation

Naturally-occurring polyelectrolytes, such as alginates, have been studied extensively for the microencapsulation of biologically-active species. The interest in these polymers arises from the fact that they can be crosslinked to hydrogels by ionic crosslinking in the presence of a divalent cation such as Ca^{++}. However, a severe need existed for a synthetic replacement for alginate, with reproducible chain length, low toxicity, and a higher loading of crosslink sites, such as carboxylic acid units.

Such a polymer has been designed and developed through a joint rersearch program between our group and the group of Robert Langer at M.I.T. The polymer is an aryloxyphosphazene with a carboxylic acid function at the para-position of every aryloxy side group (Structure 15) (54-59). Polymer 15 is soluble in water as its sodium salt, but undergoes ionic crosslinking when exposed to aqueous solutions of $CaCl_2$ (Scheme IX). Using appropriate equipment, this process can be used for the preparation of microspheres of the crosslinked polymer and for the microencapsulation of mammalian cells, proteins, and a range of other species (Figure 2) (54-58). A long-range objective is to use the microspheres in artificial organic research or for the controlled delivery of drugs or antigens.
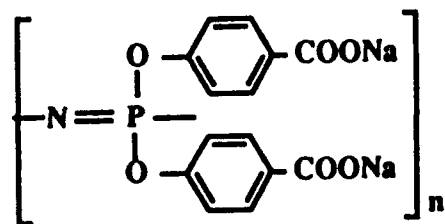
Enzyme   Enzyme   Enzyme   Enzyme
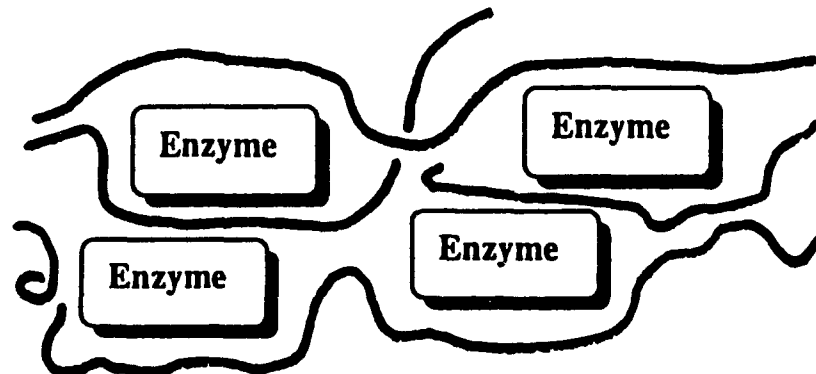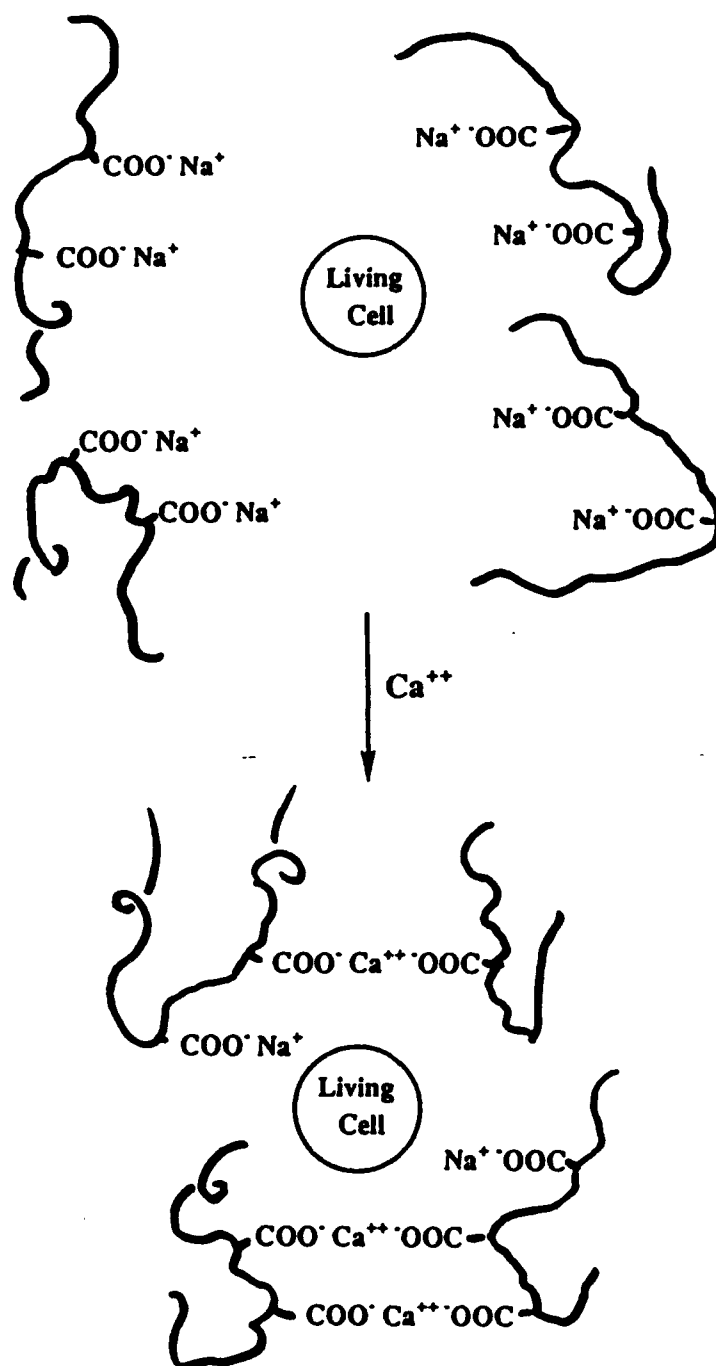
(1) Radiation crosslink matrix polymer

(2) Swell in water to form hydrogel

Enzyme   Enzyme   Enzyme   Enzyme

Scheme IX

Polymer chains
in water

Calcium ions
Link Chains
Together

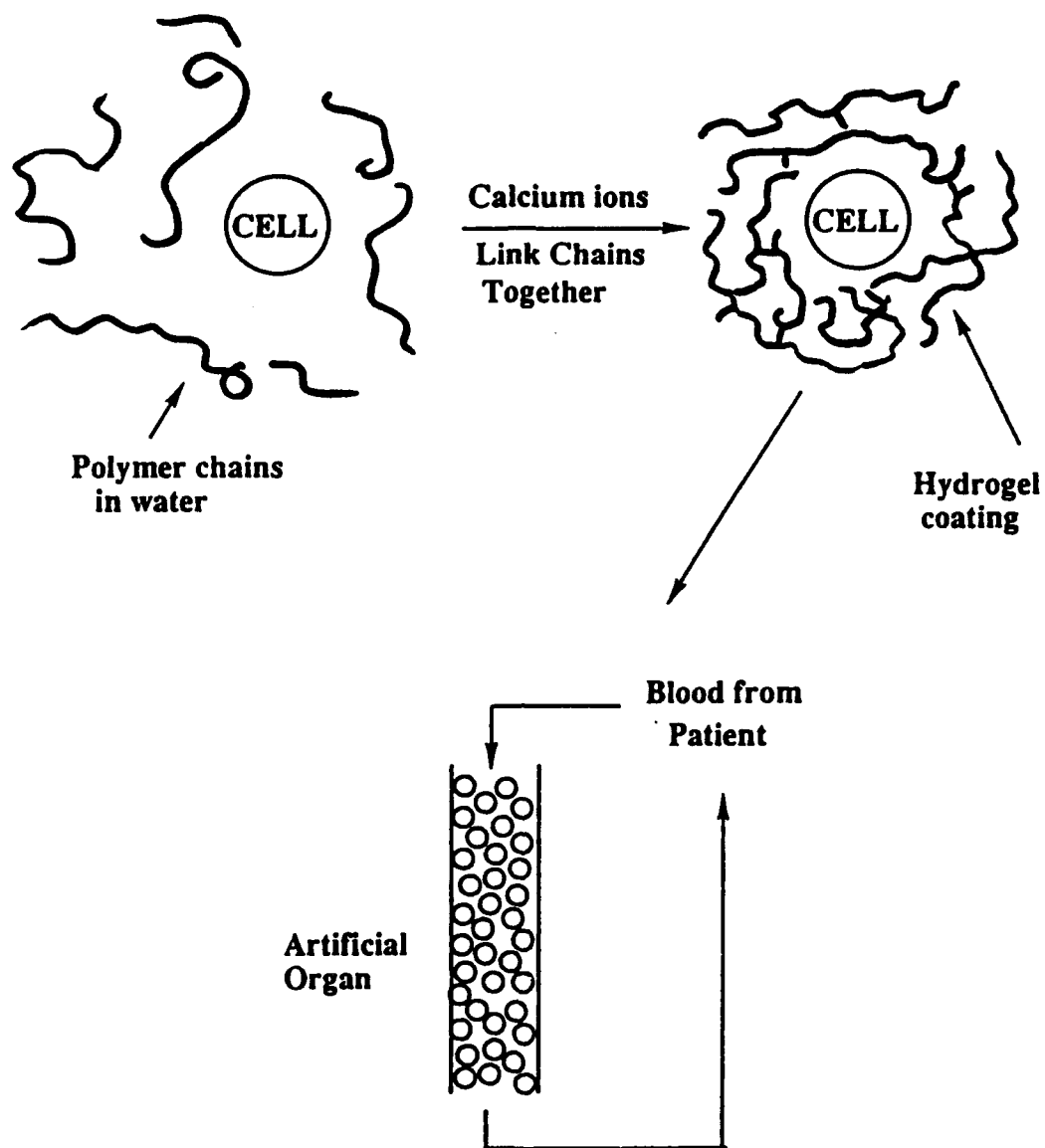CELL

CELL

Hydrogel
coating

Blood from
Patient

Artificial
Organ

Surface Reactions of Polyphosphazenes

The surface character of a polymer often controls its technological and biological properties. In the past, new surface characteristics could be generated mainly by the synthesis of entirely new polymers. The most modern approach is to choose a polymer for its "internal" properties (elasticity, rigidity, etc.) and then modify the surface by chemical reactions. We have developed a number of approaches to achieving this for polyphosphazenes (*16-20*).

First, the most important characteristic of a surface is its hydrophilicity, hydrophobicity, or amphiphilic behavior. The seven reactions shown in Scheme X illustrate approaches we have examined using hydrolysis, oxidation, sulfonation, and surface grafting to convert a hydrophobic polymer surface to a hydrophilic one. In a few of these cases, the new surface has an antibacterial character, which is important for the use of polymers in surgery.

A second type of polyphosphazene surface reaction is illustrated in Scheme XI (*59*). Here, poly[bis(phenoxy)phosphazene] is coated on to the surface of high surface area porous alumina particles, and phenoxy groups at the surface are first nitrated, and the nitro groups then reduced to $-OC_6H_4NH_2$ units. Enzymes, such as trypsin or glucose-6-phosphate dehydrogenase, were then linked to the surface amino groups using coupling reagents, such as glutaric dialdehyde, and the enzymes were shown to retain their activity and to be useable in continuous flow reactor devices. The wide variety of side groups available in polyphosphazenes is an asset for surface immobilizations of this type
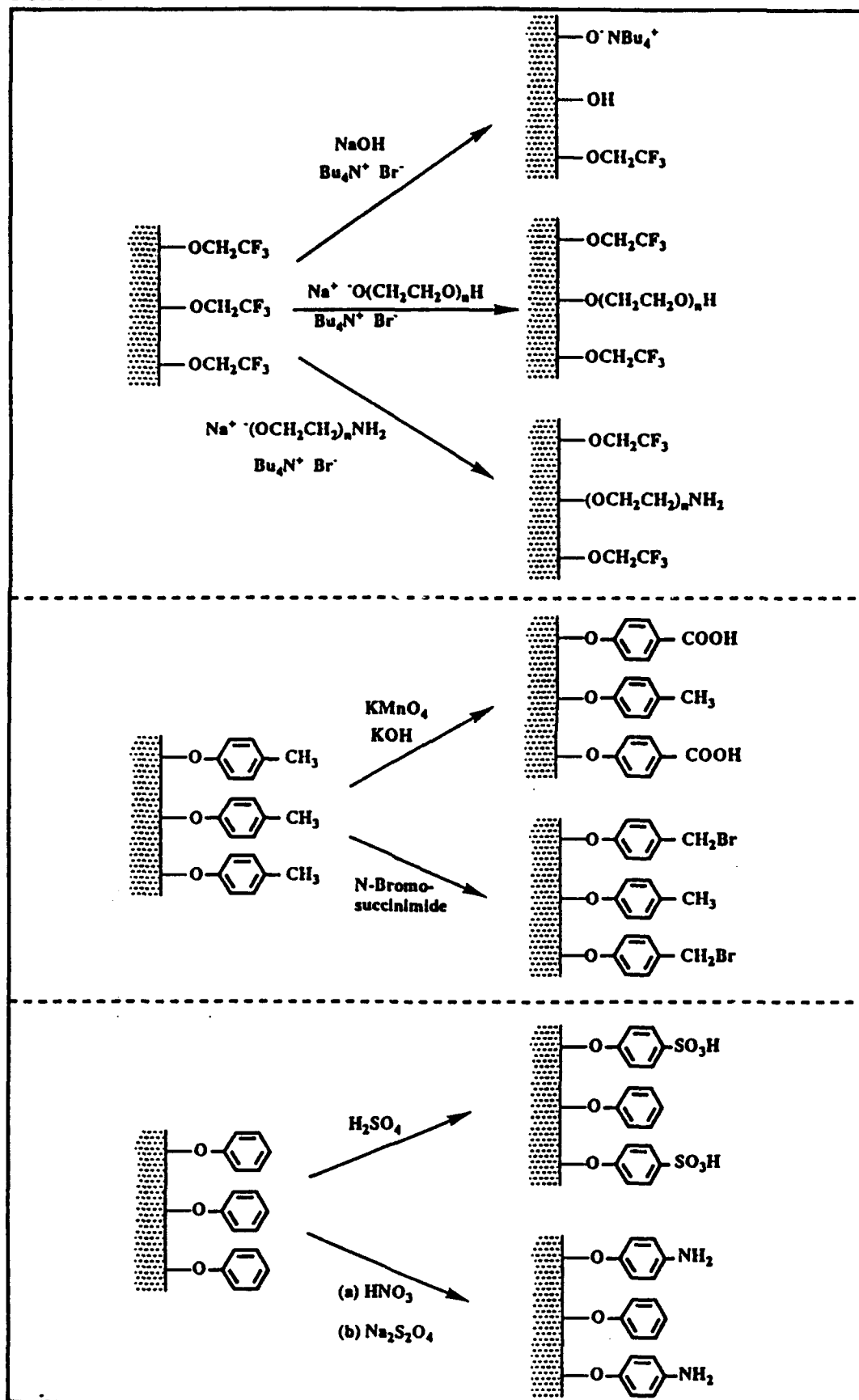
Connection to Small-Molecule Chemistry

Classical inorganic Main Group chemistry has traditionally focussed on the synthesis, reactions, and structures of small-molecule heteroatomic and homoatomic ring systems, neglecting the macromolecular and materials aspects. As an end in itself, the study of small molecule rings has become a restrictive exercise with little relevance to the wider evolution of the chemical sciences. However, the small-molecule chemistry assumes a considerably greater importance if it is viewed as model chemistry for eventual translation to the more complex macromolecular and materials fields. This is an approach that has been used in our program for many years and which has provided a continuous stream of new reactions and structural interpretations for use at the polymer and materials levels. However, it requires a willingness on the part of the small-molecule scientist to make use of often unfamiliar concepts and techniques. This is a transition that has been made by the authors of all the articles in this volume, and it is hoped that the examples given here will encourage others to follow the same path.
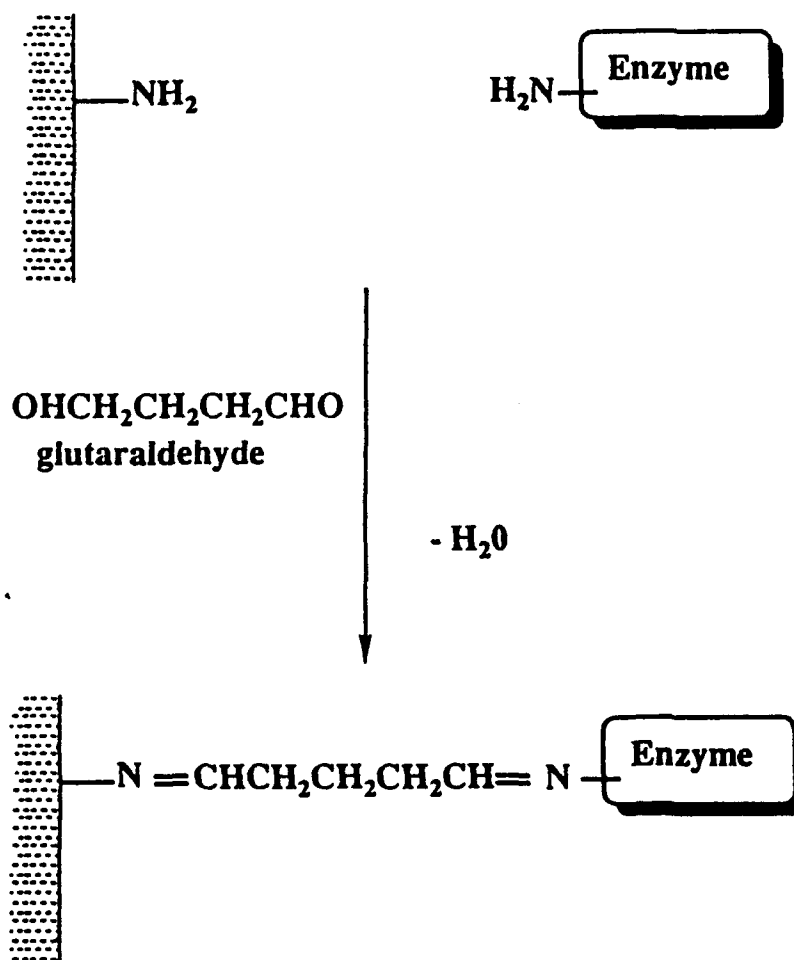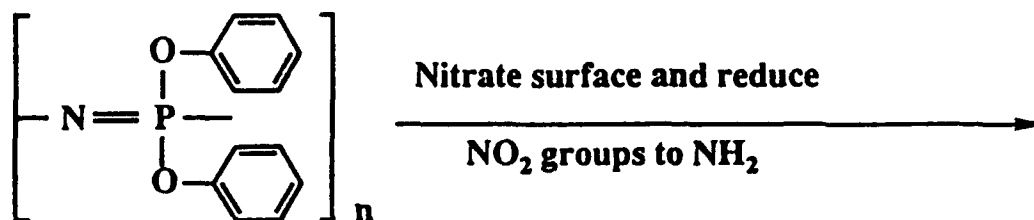
Acknowledgment

Scheme X

Scheme XI

$$\left[-N = P - \begin{array}{c} O-\bigcirc \\ | \\ O-\bigcirc \end{array} \right]_n$$

Nitrate surface and reduce
NO$_2$ groups to NH$_2$

$\longrightarrow$

—NH$_2$

H$_2$N—[Enzyme]

OHCH$_2$CH$_2$CH$_2$CHO
glutaraldehyde

- H$_2$O

$\downarrow$

—N =CHCH$_2$CH$_2$CH$_2$CH= N —[Enzyme]

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Figure 1. Gel-entrappment of enzymes such as urease.

Figure 2. Microencapsulation of biologically active species, such as mammalian cells, using ionic crosslinking of a phosphazene polyelectrolyte